1

THERMAL ANALYSIS INSTRUMENT

BACKGROUND OF THE INVENTION

The present invention relates to a thermal analysis instrument which receives a signal indicating changes in a physical or chemical property of an unknown sample and measures the signal as a function of the unknown sample with respect to temperature or time and, more particularly, to a differential scanning calorimeter (DSC) in which the aforementioned measured signal represents a differential thermal flow between the unknown sample and a reference sample.

U.S. Pat. No. 5,224,775 discloses a method and apparatus for separating a signal obtained from a heat flux DSC into a reversible component and an irreversible component by subjecting linear temperature control of an unknown sample to AC modulation. While ordinary DSC instruments control the temperature of an unknown sample linearly, the direct object of the above-mentioned patent is to divide a DSC signal into a component reflecting a reversible phenomenon and a component reflecting an irreversible phenomenon. For this purpose, the sample temperature is AC modulated, and the obtained signal is demodulated and analyzed.

On the other hand, an AC calorimeter measures minute temperature variations of an unknown sample when minute thermal vibrations are given to the unknown sample, and determines the heat capacity of the unknown sample according to the ratio between the amplitude of the quantity of heat acting as a stimulus and the amplitude of the sample temperature acting as a response. With respect to this AC calorimeter, the following papers are known: Hatta et al., "Studies on Phase Transitions by AC Calorimetry," Japanese Journal of Applied Physics, Vol. 20, No. 11, 1981, pp. 1995–2011; Dixon et al., "A differential AC Calorimeter for Biophysical Studies," Analytical Biochemistry, Vol. 121, pp. 55–61.

A DSC signal becomes a powerful tool when a physical or chemical change of an unknown sample is analyzed in relation to temperature. The DSC signals contain both information about the heat capacity of the unknown sample and information regarding its latent heat. In one method, the specific heat of the unknown sample is found from the DSC signal when no latent heat is present. In another known method, a baseline is drawn empirically to remove the component reflecting the heat capacity of the unknown sample from the DSC signal and thus the latent heat of the unknown sample is correctly found. These and other known methods have enjoyed wide acceptance. However, when the nature of the unknown sample which provides complex data about behaviors of the heat capacity and latent heat is interpreted, possibly empirical elements as described above are involved. Therefore, the nature of the unknown sample is frequently misinterpreted. It is considered that the cause of this drawback arises from the fact that when the DSC instrument itself is producing a signal, the instrument does not separate a component associated with the heat capacity of the unknown sample from a component associated with the latent heat of the unknown sample. It is expected that if the instrument can automatically perform this separation or discrimination, then the aforementioned human errors in interpretation of signals will decrease greatly. This is just the problem that the present invention is intended to solve.

The signal from the AC calorimeter does not contain any component attributed to the latent heat of the unknown sample. With respect to this, the above-cited paper by Hatta et al. describes a technique in conjunction with FIG. 14 of

2

that paper. In particular, results of the DSC are compared with results of the AC calorimeter. A component reflecting the heat capacity of the unknown sample is found from the latter results. A component reflecting the latent heat of the unknown sample is found from the difference between the former results and the latter results. In this case, the same sample is investigated by two kinds of instruments, i.e., the DSC and the AC calorimeter, separately. Then, their results must be compared. In this way, cumbersome operations are needed.

On the other hand, the instrument disclosed in U.S. Pat. No. 5,224,775 is claimed to divide the DSC signal into both a reversible component and an irreversible component. However, a careful consideration of the disclosure in that patent reveals that the technique used to derive the reversible component very closely resembles the method of determination of the heat capacity in the AC calorimeter. Hence, there is the possibility that this technique becomes a means for solving the above-described problem.

However, as disclosed in that patent specification, the instrument is based on the so-called heat flux DSC structure. In particular, the temperature difference between the unknown sample and the reference sample is transformed into the difference between two heat flows, one of which is directed from the unknown sample to a heat reservoir, the other being directed from the reference sample to the heat reservoir. Then, the heat flow difference is measured. In principle, only the temperature difference between the unknown sample and the reference sample is measured.

Hence, the AC heat capacity of the unknown sample cannot be found precisely for the following reason. In order to determine the differential heat capacity between the unknown sample and the reference sample, it is necessary to find the difference between the heat flow amplitude on the side of the unknown sample and the heat flow amplitude on the side of the reference sample. This difference cannot be measured precisely unless these AC heat flows are in phase. In practice, during measurement, if the unknown sample causes a transition such as melting, the phase of the AC heat flow on the side of the unknown sample varies greatly. This makes it impossible to precisely measure the AC heat capacity of the unknown sample.

The inventors of the above-described patent, and others, state that melting of polyethylene terephthalate was measured with an instrument based on the aforementioned patent and that melting of microscopic structures inside the unknown sample and recrystallization were observed, based on the behavior of the separation into a reversible component and an irreversible component. Nonetheless, our experiment has demonstrated that the behavior of separation into the reversible component and the irreversible component can be varied simply by changing the quantity of the reference sample, irrespective of the nature of the unknown sample. Consequently, in measurement of such a system, a signal obtained based on the above patent reflects neither the heat capacity of the unknown sample nor the nature itself of the unknown sample.

This situation can be easily understood from considerations, using the diagram shown in FIG. 2 of the accompanying drawing, bracketed [ ] terms are vectors. Specifically, [Ts] is a vector indicating the AC temperature of an unknown sample. [Tr] is a vector indicating the AC temperature of a reference sample. $[dT]=[Ts]-[Tr]$ is a temperature difference signal which is an archetype of the DSC signal from a heat flux DSC. Generally, if [Ts] and [Tr] differ in sense, we have the relationship